Crystal structure of rubidium bis(salicylato)borate, $Rb[B(OC_7H_4COO)_2]$

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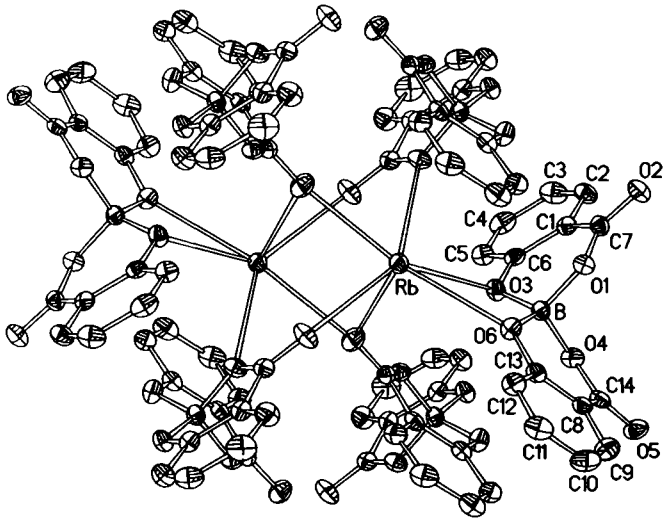

Abstract

$C_{14}H_8BO_6Rb$, monoclinic, $P12_1/c1$ (no. 14),
$a = 11.5889(6)$ Å, $b = 7.8521(4)$ Å, $c = 15.7120(8)$ Å,
$\beta = 108.816(2)°$, $V = 1353.4$ Å^3, $Z = 4$,
$R_{gt}(F) = 0.062$, $wR_{ref}(F^2) = 0.174$, $T = 293$ K.

Source of material

Salicylic acid (11.04 g, 0.08 mol) was dissolved in mixed solvent (20 ml water and 20 ml ethanol) under heating and magnetically stirring to give clear solution. Boric aid H_3BO_3 (2.47 g, 0.04 mol) was dissolved in water (20 ml) under heating to prepare clear solution (pH = 4-5). The latter solution was added dropwise under strong stirring to the first one at about 50-70 °C. Finally, Rb_2CO_3 (9.25 g, 0.04 mol), divided into many small batches, was carefully added into the above solution, until no bubbles escaped, and a colorless and clear solution (pH = 5-6) was obtained. After gravity filtering, the filtrate was allowed to stand for about 60 days at room temperature, whereupon transparent and fine crystals were harvested (yield 90 %).

Discussion

For the past few decades, a lager number of inorganic borates have been synthesized and characterized. These borates exhibit a series of unusual physical and chemical properties, ranging from nonlinear optical properties of β-BaB_2O_4 (β-BBO) [1] to the catalytic activity of $Cu_2Al_6B_4O_7$ [2], which have attracted more and more attention of researchers in many scientific and technological fields. However, in comparison with inorganic borates the corresponding investigations involving organic borates seem insufficient in the areas of either theoretical exploration (synthesis, structure determination) or application. The crystal structures and synthesizing methods of l-malato- and 2,3-dihydroxy-naphthalene borates were reported [3-5], but the structures and syntheses of organic borates, especially containing the extremely reactive alkali-metals are still in a tiny minority. As part of our efforts to synthesize and characterize new borates, we recently succeeded in synthesizing $Rb[B(C_7H_4O_3)_2]$, a novel rubidium organic borate.

The crystal structure of the title compound is isotypic to the structure of the analogous Cs compound [4]. The basic structure framework of $Rb[B(C_7H_4O_3)_2]$ consists of one set of distorted $[BO_4]$ tetrahedron and two sets of slightly deformed $[C_7H_4O]$ planes with oxygen atoms as sharing vertices. The sp^3-hybridized B atom is bonded to four oxygen atoms to form a tetrahedral environment. Each $[C_7H_4O]$ unit is nearly planar, and both $[C_7H_4O]$ units in $Rb[BO_4(C_7H_4O)_2]$ are almost perpendicular to each other. The Rb^+ ion is coordinated by six O atoms ($O2^{\#4}$, $O2^{\#1}$, $O3^{\#3}$, O4, $O5^{\#2}$, $O6^{\#3}$) and surrounded in further coordination spheres by one oxygen atom (O5), three carbon atoms (C5, C6, C14), one boron atom ($B^{\#3}$) and one Rb ($Rb^{\#2}$) to form a weak interaction coordination environment (#1 – #5: symmetry codes according to symmetry and coordinates in the CIF file). The Rb—O bond lengths range from 2.855(5) Å to 3.048(5) Å with an average value of 2.962 Å. The ionic and molecular units form a 2D structure with layers parallel to the b,c plane.

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.22 × 0.60 × 0.80 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	36.85 cm^{-1}
Diffractometer, scan mode:	Siemens SMART 1000 CCD, φ/ω
$2\theta_{max}$:	50.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3684, 2352
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2005
$N(param)_{refined}$:	199
Programs:	SHELXTL [6], ORTEP-3 [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2A)	4e	0.7018	0.6427	0.5099	0.050
H(3A)	4e	0.8836	0.5321	0.5043	0.062
H(4A)	4e	0.8899	0.3703	0.3837	0.059
H(5A)	4e	0.7162	0.3472	0.2572	0.049
H(9A)	4e	0.0429	0.1106	0.2977	0.061
H(10A)	4e	–0.1266	0.1698	0.1745	0.068
H(11A)	4e	–0.1038	0.3379	0.0616	0.060
H(12A)	4e	0.0803	0.4521	0.0696	0.052

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb	4*e*	0.60134(6)	0.06054(9)	0.43515(4)	0.0362(4)	0.0440(4)	0.0303(4)	0.0062(3)	0.0095(3)	0.0026(3)
O(1)	4*e*	0.3792(4)	0.5550(6)	0.3316(3)	0.030(2)	0.034(2)	0.038(3)	0.003(2)	0.006(2)	–0.001(2)
O(2)	4*e*	0.4719(5)	0.7301(7)	0.4428(4)	0.056(3)	0.048(3)	0.044(3)	–0.003(3)	0.014(2)	–0.017(3)
O(3)	4*e*	0.4964(4)	0.4023(7)	0.2516(3)	0.027(2)	0.055(3)	0.029(2)	–0.006(2)	0.004(2)	–0.009(2)
O(4)	4*e*	0.3801(4)	0.2517(6)	0.3275(3)	0.031(2)	0.037(3)	0.035(2)	0.001(2)	–0.004(2)	0.005(2)
O(5)	4*e*	0.2759(5)	0.0842(7)	0.3874(3)	0.062(3)	0.044(3)	0.036(3)	–0.015(3)	0.003(2)	0.011(2)
O(6)	4*e*	0.2846(4)	0.4177(6)	0.1918(3)	0.025(2)	0.048(3)	0.028(2)	–0.001(2)	–0.001(2)	0.007(2)
C(1)	4*e*	0.5958(6)	0.5407(8)	0.3913(4)	0.036(4)	0.033(4)	0.025(3)	–0.003(3)	0.001(3)	0.007(3)
C(2)	4*e*	0.7035(7)	0.5759(9)	0.4614(5)	0.044(4)	0.039(4)	0.034(4)	0.000(3)	0.000(3)	–0.005(3)
C(3)	4*e*	0.8119(7)	0.510(1)	0.4576(6)	0.038(4)	0.051(5)	0.050(4)	–0.001(4)	–0.009(3)	0.001(4)
C(4)	4*e*	0.8157(7)	0.413(1)	0.3855(6)	0.030(4)	0.053(5)	0.059(5)	–0.001(3)	0.007(3)	0.014(4)
C(5)	4*e*	0.7097(6)	0.377(1)	0.3160(5)	0.036(4)	0.042(4)	0.042(4)	0.001(3)	0.010(3)	0.001(3)
C(6)	4*e*	0.6005(6)	0.4404(8)	0.3193(4)	0.026(3)	0.034(3)	0.031(3)	–0.006(3)	0.003(3)	0.004(3)
C(7)	4*e*	0.4783(6)	0.6154(9)	0.3916(4)	0.042(4)	0.034(4)	0.027(3)	0.004(3)	0.009(3)	0.000(3)
C(8)	4*e*	0.1654(6)	0.2432(9)	0.2574(4)	0.032(3)	0.033(3)	0.032(3)	–0.006(3)	0.007(3)	–0.007(3)
C(9)	4*e*	0.0510(7)	0.179(1)	0.2515(6)	0.045(4)	0.052(5)	0.055(5)	–0.002(4)	0.016(4)	0.006(4)
C(10)	4*e*	–0.0506(7)	0.214(1)	0.1782(6)	0.028(4)	0.057(5)	0.078(6)	–0.013(4)	0.009(4)	–0.005(5)
C(11)	4*e*	–0.0363(6)	0.315(1)	0.1115(6)	0.029(4)	0.049(4)	0.057(5)	0.005(3)	–0.005(3)	–0.002(4)
C(12)	4*e*	0.0736(6)	0.382(1)	0.1157(5)	0.034(4)	0.050(4)	0.037(4)	–0.002(3)	0.001(3)	0.004(3)
C(13)	4*e*	0.1760(6)	0.3462(9)	0.1895(4)	0.026(3)	0.041(4)	0.031(3)	–0.003(3)	0.004(3)	–0.007(3)
C(14)	4*e*	0.2765(6)	0.1850(8)	0.3300(4)	0.038(4)	0.028(3)	0.029(3)	–0.004(3)	0.003(3)	–0.006(3)
B	4*e*	0.3845(7)	0.406(1)	0.2753(5)	0.033(4)	0.038(4)	0.023(3)	–0.002(3)	0.004(3)	0.000(3)

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